# Diamondoids in octahedral iron complexes: A DFT study

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## ABSTRACT

Several octahedral iron complexes that contain two lateral diamondoid (formerly called nanodiamond) units (joined by terminal $COO^{1-}$ groups) have been proposed. All newly proposed coordination species reach a stable configuration. The nature of the apical substituents ($H_2O$, $NH_3$, CO, $CN^{1-}$, NO) accounts for the change in properties of the resultant compounds, therefore those compounds containing $H_2O$ or $NH_3$ ligands manifest a scheme of chemical properties similar to their analogues as coordination compounds. Furthermore the complexes containing CO or $CN^{1-}$ ligands fulfill the typical description of organometallic species, whereas the complexes with the NO ligand, in their three manifestations, range between both behaviors and are studied as a special case. However, in all cases, the diamondoid ligands work as insulator walls restricting electronic movements to the regions which accommodate the metallic center, the apical ligands and the terminal $COO^{1-}$ groups. The nature of the molecular orbitals scheme shows wide variation that ranges between insulator and conductor behavior.

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## 1. Introduction

Since the first studies addressing the existence and characterization of nanodiamonds [1], this carbon nanostructure has fascinated the scientific community [2]. The possibility of the existence of coordination compounds of nanodiamond has been studied [3]. Their chemical features are particularly interesting because these compounds display both normal behavior; where nanodiamond acts as an insulator, but in some cases the inner carboxylated substituted iron complexes exhibit conductor characteristics. The characteristic behavior of these structures lies in their absence of symmetry because of the tetracoordinated complex that is proposed for these substances; an attribute not widely known in the case of iron complexes.

Iron is a notably versatile transition metal for preparing coordination compounds [4]. The most common coordination number is six [5], although distortions are also common [6]. Four coordination compounds are known to exist and are mainly compounds that contain porphyrin, salicyldiminato and phthalocyanine ligands but also other known cases of tetrahedral complexes [7].

A previous publication on this topic [3], discussed only those structures with coordination number four because the main interest was to study the direct possibility and the effect of nanodia-

mond as a ligand on this type of coordination compound. Therefore, only the covalent coordinated bonds linking the oxygen atoms to the iron center were considered. Note that the specific geometry was a distortion of the ideal planar geometry (it would be a $D_{2d}$ point group if only the Fe atom and two carboxylate groups ($COO^{1-}$) were considered). However, the best known geometry in the case of iron complexes is that of octahedral compounds. It is thus interesting to study these derivatives, considering that different substituents may complete the coordination sphere in this case.

Considering this, the main goal of the present work is to model a set of coordination compounds where the common factor is the framework of a tetrahedral compound of two lateral nanodiamond units that are joined to a central Fe atom using ($COO^{1-}$) groups. It is important to specify that in our nomenclature, nanodiamond is the term used to refer to diamonds with a size below 1 µm. In the present case, the fragments being studied have sizes around 20 Å which are derivatives of adamantane [8], so that the name of these fragments should in fact be diamondoids; thus this term will be used throughout this paper. Furthermore, there are other definitions of nanodiamond that refer to a diamond-like core covered with a fullerene-like shell [9,10]. This model was not used in our case and is only cited in order to expand our definition.

Several common ligands complement the octahedral coordination, around the framework. These combinations can form the

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classical coordination species when the substituent is water ($H_2O$), ammonia ($NH_3$), or carbon monoxide (CO) as neutral ligands, cyanide ($CN^{1-}$) as an anion and the more sophisticated case of nitrosyl in different forms. The particular substituents were selected based on their varied behavior because the fragments that follow the conventional coordination chemistry can be compared with organometallic or catalytic substituents with reference to their ability to achieve a nanodiamond effect. The general shape is shown in Fig. 1.

The previous study [3] showed that these compounds have interesting electronic properties with potential applications as electronic devices. This possibility arises because of an electronic confinement effect which is caused by the presence of both diamondoid "walls" (we have named this phenomenon "nanodiamond effect") together with the effect of different substituents. An important aspect to consider in this study concerns the consequences of quantum confinement on the substituted diamondoid complexes.

## 2. Computational details

A detailed structure study for different Fe complexes, such as: $FeC_{46}H_{54} \cdot 2(H_2O)$, $FeC_{46}H_{54} \cdot 2(CO)$, $FeC_{46}H_{54} \cdot 2(CN^{1-})$, $FeC_{46}H_{54} \cdot 2(NH_3)$, $FeC_{46}H_{54} \cdot 2(^1NO)$ (neutral singlet), $FeC_{46}H_{54} \cdot 2(^3NO)$ (neutral triplet) and $FeC_{46}H_{54} \cdot 2(^1NO^{1-})$ (anion singlet), has been carried out using ab initio quantum chemical methods. The electronic structure of these compounds has been studied within the framework of the hybrid density functional theory, for energy evaluations, to which Becke's gradient corrections [11] for exchange and Perdew–Wang's for correlation were applied [12]. This scheme gives place to the B3PW91 method, which forms part of the Gaussian09 code [13]. All calculations were performed using the 6-31G** basis set. The convergence criterion used was $1 \times 10^{-8}$ a.u. for the Maximal Residual Force. Prior to optimization, we undertook a conformational search for all complexes studied. Frequency calculations were carried out at the same level of theory to confirm that the optimized structures were at a minimum of the potential surfaces.

The electronic structure and several properties were obtained and analyzed. These include the widely used frontiers orbital, HOMO, LUMO, HOMO–LUMO energy gap ($\Delta_{HOMO-LUMO}$), electrostatic potential, electric dipole moments, isotropic polarizabilities and spin density. Likewise we studied the energy stability of these Fe complexes.

## 3. Results and discussion

The shape of all compounds that are included corresponds to the general framework in Fig. 1. Each case is described separately according to its intrinsic nature, i.e., the compounds without an Fe–C bond are simply considered as coordination compounds whereas those with an Fe–C bond are classified as organometallic compounds. There are two pure coordination compounds (which contain $H_2O$ and $NH_3$ ligands), two organometallic complexes (which correspond to CO and $CN^{1-}$ as ligands) and the complex that contains nitrosyl which is not a well-defined case, (the nitrosyl complex). The complex that contains nitrosyl ligands was localized at a point between the two descriptions, and must therefore be considered a special case.

The optimized geometrical parameters for different Fe complex (Fig. 1) calculated at B3PW91/6-31G** level theory are displayed in Tables 1a and 1b. Table 1a shows the bond distances of C–C (R) of the ($COO^{1-}$) on the square plane; the Fe–O, and Fe–L. The differences between the distances for different ligands are in the order of $10^{-1}$ Å. The distances Fe–L, where L = $H_2O$, $CN^{1-}$, $NH_3$, CO, $^1NO_{neutral}$, $^3NO_{neutral}$, $^1NO^{1-}$ are 2.00 Å; 1.99 Å; 1.95 Å, 1.84 Å, 1.83 Å; 1.77 Å, and 1.6 Å. The distances for Fe–$H_2O$ and Fe–$NH_3$ are larger because these ligands are electron-donor groups, whereas the distances Fe–CO, and Fe–NO are shorter as these ligands are electron accepting groups. Notably all the Fe complexes studied present an $O_h$ point group. Evidently, the effect of the octahedral coordination for diamondoid is reflected in the bond distance between the Fe atom and the carbon of the ($COO^{1-}$) groups; this distance is shorter for $H_2O$, CO, $NH_3$, and longer for $CN^{1-}$, $^1NO$, $^3NO$ of the pure diamondoid. In the case of the NO complex anion singlet ($^1NO^{1-}$) the effect of the negative charge is reflected in a substantial bond distance between the ($COO^{1-}$) group and the diamondoid fragment. The bond distance $H_2O$–Fe is large, reflecting a relatively weak bond. In spite of the negative charge of the ligands $CN^{1-}$ and $^1NO^{1-}$, these complexes have the opposite effect, the distance between Fe and $CN^{1-}$ is relatively large (1.99 Å) and the equivalent for $^1NO^{1-}$ is smaller (1.6 Å); this result indicates the effect of the electronic distribution on the ligand, the electron density in $CN^{1-}$ complex is found on N atom whereas in the $^1NO^{1-}$ complex the electron density is on the terminal oxygen atom. Table 1b shows selected angles indicative of the distortion in the compounds with NO ligand.

## 4. Thermodynamic stability

In order to analyze the relative stability of the proposed compounds, we estimated energetic stability as a function of the energy calculated according to the expression:

$$E_f = \left( E_{T,diamondoid\ complex} - \sum_{i=C,H,Fe,O,N} n_i E_{T,i} \right) \Big/ X$$

where $E_{T,diamondoid\ complex}$ is the energy of the complex, $n_i$ indicates the number of atomic species per molecule and $E_{T,i}$ the total energy of
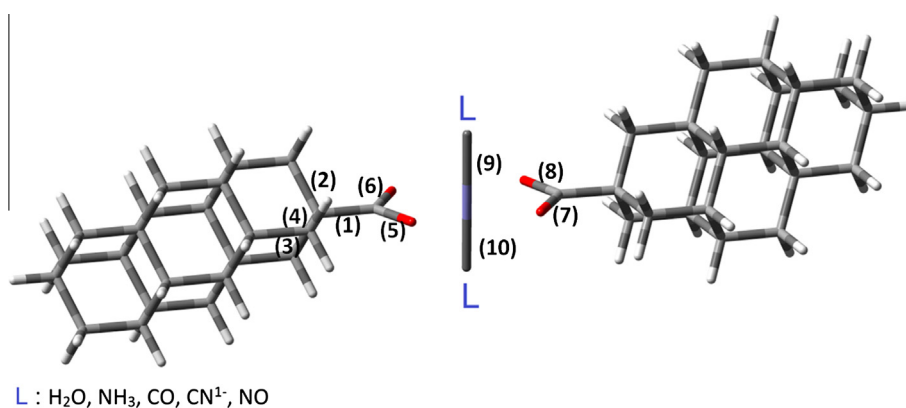


L : $H_2O$, $NH_3$, CO, $CN^{1-}$, NO

**Fig. 1.** Schematic representation and numeration of complexes formed between ($COO^{1-}$) of diamondoid with different types of ligands (L).

**Table 1a**
Bond lengths for diamondoid and different Fe complexes at the B3PW91/6-31G** level of theory. For numeration see Fig. 1.

| Bond (Å) | $C_{23}H_{30}$ | $FeC_{46}H_{54} \cdot 2(H_2O)$ | $FeC_{46}H_{54} \cdot 2(CO)$ | $FeC_{46}H_{54} \cdot 2(CN^{1-})$ | $FeC_{46}H_{54} \cdot 2(NH_3)$ | $FeC_{46}H_{54} \cdot 2(^1NO)$ | $FeC_{46}H_{54} \cdot 2(^3NO)$ | $FeC_{46}H_{54} \cdot 2(^1NO^{1-})$ |
|---|---|---|---|---|---|---|---|---|
| C–C (1) | 1.53 | 1.51 | 1.51 | 1.53 | 1.52 | 1.51 | 1.51 | 1.57 |
| C–C (2) | 1.54 | 1.55 | 1.55 | 1.53 | 1.54 | 1.55 | 1.54 | 1.54 |
| C–C (3) | 1.54 | 1.54 | 1.54 | 1.54 | 1.54 | 1.54 | 1.55 | 1.54 |
| C–C (4) | 1.54 | 1.54 | 1.54 | 1.54 | 1.54 | 1.54 | 1.54 | 1.53 |
| Fe–O(COO)$^{1-}$ (5) | | 2.00 | 2.04 | 2.02 | 2.10 | 2.00 | 1.97 | 3.41 |
| Fe–O(COO)$^{1-}$ (6) | | 2.01 | 2.02 | 2.02 | 2.06 | 1.97 | 1.98 | 2.05 |
| Fe–O(COO)$^{1-}$ (7) | | 2.00 | 2.04 | 1.27 | 2.10 | 2.00 | 1.28 | 3.41 |
| Fe–O(COO)$^{1-}$ (8) | | 2.00 | 2.02 | 1.27 | 2.06 | 1.97 | 1.28 | 2.05 |
| Fe–L (9) | | 2.00 | 1.84 | 1.99 | 1.95 | 1.77 | 1.83 | 1.60 |
| Fe–L (10) | | 2.01 | 1.84 | 1.99 | 1.95 | 1.77 | 1.83 | 1.60 |
| | | O–H (H$_2$O) (9) 0.97 | C–O (CO) (9) 1.15 | C–N (CN) (9) 1.18 | N–H (NH$_3$) (9) 1.02 | N–O (NO) (9) 1.16 | N–O (NO) (9) 1.16 | N–O (NO) (9) 1.21 |
| | | O–H (H$_2$O) (9) 0.97 | C–O (CO) (9) 1.16 | C–N (CN) (9) 1.18 | N–H (NH$_3$) (9) 1.02 | N–O (NO) (10) 1.16 | N–O (NO) (10) 1.16 | N–O (NO) (10) 1.21 |
| | | O–H (H$_2$O) (10) 0.97 | | | N–H (NH$_3$) (9) 1.02 | | | |
| | | O–H (H$_2$O) (10) 0.97 | | | N–H (NH$_3$) (10) 1.02 | | | |
| | | | | | N–H (NH$_3$) (10) 1.02 | | | |
| | | | | | N–H (NH$_3$) (10) 1.02 | | | |

**Table 1b**
Bond angles for different Fe complexes at the B3PW91/6-31G** level of theory.

| Angles (°) | $FeC_{46}H_{54} \cdot 2(H_2O)$ | $FeC_{46}H_{54} \cdot 2(NH_3)$ | $FeC_{46}H_{54} \cdot 2(CO)$ | $FeC_{46}H_{54} \cdot 2(CN^{1-})$ | $FeC_{46}H_{54} \cdot 2(^1NO)$ | $FeC_{46}H_{54} \cdot 2(^3NO)$ | $FeC_{46}H_{54} \cdot 2(^1NO^{1-})$ |
|---|---|---|---|---|---|---|---|
| L–Fe–L[a] | 169.302 | 179.447 | 178.922 | 179.472 | 161.803 | 179.09 | 109.698 |
| Fe–N–O | | | | | 124.361 | 132.078 | 163.815 |
| C(COO$^{1-}$)–Fe–C(COO$^{1-}$) | 177.781 | 178.317 | 178.332 | 177.812 | 176.312 | 178.432 | 118.198 |

[a] Measured between central atom from ligand to Fe atom.

the molecular form of H$_2$, N$_2$, O$_2$ and atomic C and Fe calculated with the same model and basis for the optimized structures and $X$ is the total number of atoms for each complex. Table 2 shows the resulting energy.

As apparent, all studied compounds are thermodynamically stable. In the case of the NO complex, the energy differences are so small that it may be present in all three different electronic states: neutral singlet, neutral triplet and anion singlet. The energy for the relative stability of the diamondoid fragment is included as reference. Evidently, the pure coordination compounds are the less stable species, whereas the organometallic compounds represent more stable species when compared with the pure diamondoid fragment.

## 5. Electrical polarity and polarizability

The behavior of molecules when electrical field is applied produces interesting results because there are many theoretical and experimental studies focusing on the nonlinear optical (NLO) properties of molecules that result from their potential technical appli-

cation governed at the microscopic level by their polarizability [14,15].

Table 3 shows the electric dipole moment as well as isotropic polarizability for all studied complexes. The diamondoids act as a barrier and consequently the charge separation has been surpassed only by the ligands. The complex with the highest dipole moment is the case where water is a ligand, not including the anions. Evidently, the value for polarizability varies between diamondoid and the various complexes. For the purpose of comparison the isotropic polarizability per atom values are also included, indicating the influence of the ligands on the ability of the complex to be polarized.

As apparent in the table, the diamondoid has the lowest value in terms of polarizability per atom; hence the effect of the ligands is in all cases, to increase the ability of the molecules to be polarized. The case of the anions must be carefully considered, due to the presence of an explicit negative charge.

**Table 2**
Relative energy for all studied complexes.

| Ligand | Relative stability energy per atom (kcal/mol) |
|---|---|
| H$_2$O | −103.29 |
| CO | −108.61 |
| NH$_3$ | −100.86 |
| $^1$NO | −103.82 |
| $^3$NO | −103.82 |
| $^1$NO$^{1-}$ | −103.97 |
| CN$^{1-}$ | −107.23 |
| C$_{23}$H$_{30}$ | −103.08 |

**Table 3**
Electric dipole moment, isotropic polarizability and isotropic polarizability per atom for all studied complexes.

| Ligand Diamond | Electric dipole moment ($D$) | Isotropic polarizability (Bohr$^3$) | Isotropic polarizability per atom (Bohr$^3$) 5.5 (experimental) [14] |
|---|---|---|---|
| C$_{23}$H$_{30}$ | 0.0998 | 210.78 | 3.97 |
| H$_2$O | 2.9999 | 476.17 | 4.29 |
| CO | 0.1268 | 496.23 | 4.55 |
| CN$^{(1-)}$ | 1.2877 | 503.25 | 4.62 |
| NH$_3$ | 0.1607 | 483.97 | 4.28 |
| $^1$NO | 0.0385 | 504.29 | 4.62 |
| $^3$NO | 0.1228 | 500.25 | 4.59 |
| $^1$NO$^{1-}$ | 29.5337 | 505.32 | 4.64 |

## 6. H₂O and NH₃ complexes

These complexes show similar behavior, the frontier molecular orbitals and their respective energy differences are shown in Fig. 2. The eigenvalues for all the orbitals in both species are found approximately in the same region. The energy of the HOMO–LUMO gap is 4.5 eV for the water derivative and 4.3 eV for the ammonium derivative. Both species exhibit insulator characteristics as a result of this feature.

The shape and distribution of these orbitals can provide important information about their reactivity. In this sense, both species appear to have similar characteristics. For the water derivative the HOMO is mainly a localized orbital that is centered in the region of the iron atom and its bonds toward the ligands. This function is relatively similar to that of the tetrahedral species [3] although the new ligands (both water molecules) also participate in the present instance. The main difference is that the water derivative acts as an insulator species because the LUMO is distant in terms of energy, and spontaneous electronic transfers are not expected.

In contrast with previous results [3], the LUMO has a more diffuse function. Innovatively, this involves the first carbon atoms of the diamondoid ligand. This feature can drastically change the chemical characteristics in this species because an electrophilic process is able to take place in this region of the molecule. The tetrahedral compounds do not have this possibility.

The situation is similar in the case of the ammonium complex. The HOMO is localized at the center and involves the iron, $(COO^{1-})$ terminals and new ligands. However, the new situation is that the ammonium ligands are "activated", i.e., it appears relatively easy to donate protons from this ligand probably because of the behavior of free ammonium. The LUMO again fulfills a delocalized function and also involves the first neighbor carbon atoms of the diamondoid ligand. This ammonium complex should thus represent a good electrophilic agent.

Fig. 3 shows the electrostatic potentials of the ammonium derivative and ammonium molecule which were measured on the hydrogen atoms of the NH₃ group. This comparison was made because ammonium as a compound is a common reactive in organic chemistry and organic cations or radicals can easily substitute its hydrogen atoms. Fig. 3 shows a large positive electrostatic potential for the hydrogen atoms of the studied compound. Therefore, the ammonium complex should participate in organic reactions with an identical level of activity as free ammonium; however its behavior appears to be more aggressive.

## 7. CO and CN$^{1-}$ complexes

These two ligands give place to organometallic species and show notably different behaviors from each other, as well as compared to the other cases.
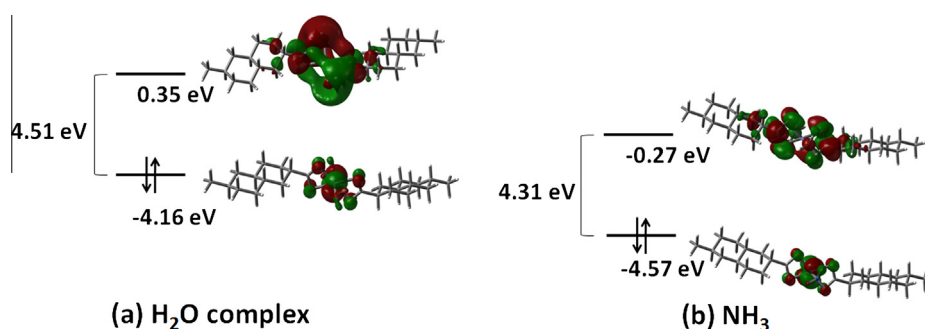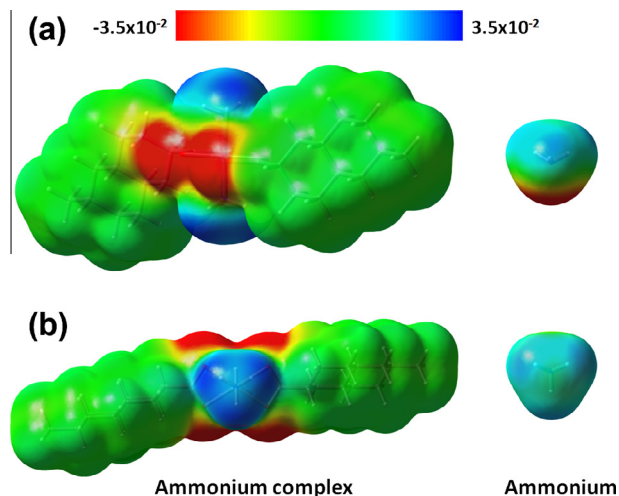


**Fig. 3.** Electrostatic potential over the electron density of the ammonium complex compared with the ammonium molecule, where L = NH₃ according to Fig. 1. (a) Lateral view of the ammonium complex and molecule; (b) front view.

The shape and energy values of the frontier molecular orbitals of the carbonyl complex are shown in Fig. 4a. Both orbitals are localized in a deeper energy region with respect to the "coordination examples", the energy gap between HOMO and LUMO is approximately 5 eV; therefore, it is also an insulator species. The HOMO is localized at the center and the orbital is distributed on the iron atom and all ligands. The classical well-known back-bond effect, studied for carbonyl metallic complexes [16] is not found in this case because the iron atom has limited participation in the LUMO, as shown in Fig. 4a. However, there is a remarkable phenomenon with respect to this particular orbital. First, the orbital is actually a sum of LUMO and LUMO + 1 functions because an accidental degeneration takes place. The point group of the molecule is only a C₂ which does not have double degenerated irreducible representations. These eigenvalues are so close in terms of energy values that they can be considered to constitute a double folded degenerated set. This behavior arises from the symmetry of the isolated center of the molecule; the iron atom can be considered the center of a little fragment that is surrounded by four oxygen atoms in the equator and two carbonyl groups in the apex. This fragment belongs to the D₄ₕ point group which presents two folded degenerated irreducible representations. This description implies that it should not be considered as the large bulk of both terminal diamondoid ligands; however, they appear to function as insulators. Therefore, the central atoms are constrained and isolated by the insulator walls in some manner and manifest individual behavior; a similar description was found in the study of tetrahedral diamondoid derivatives with respect to electronic flows [3].
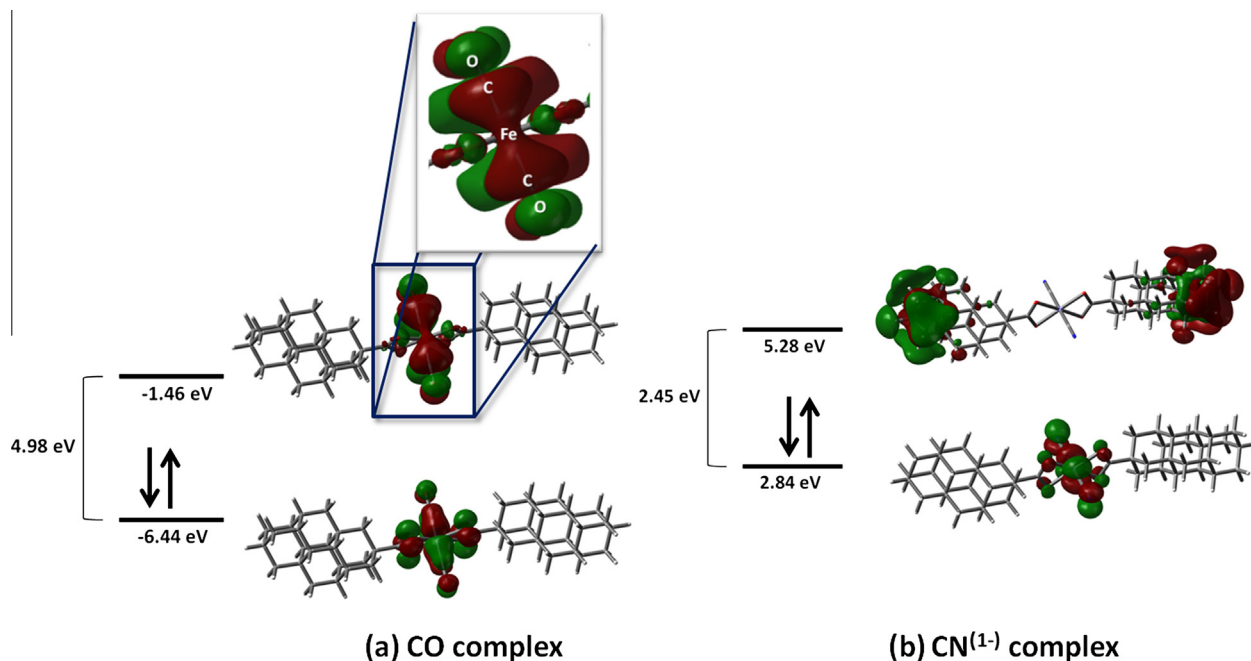


**Fig. 2.** Frontier orbital diagram of the octahedral diamondoid complex with: (a) L = H₂O and (b) L = NH₃. The HOMO–LUMO energy gap is shown.

**Fig. 4.** Frontier orbital diagram of the octahedral diamondoid complex with: (a) L = C0 and (b) L = CN$^{1-}$. The HOMO–LUMO energy gap is shown.
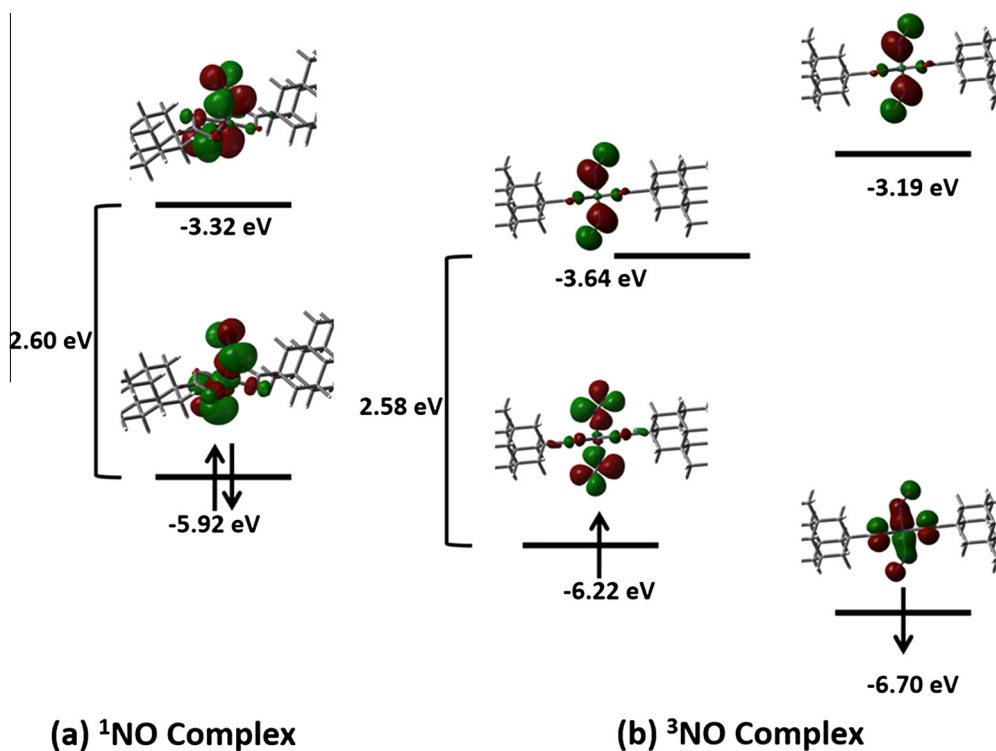


**Fig. 5.** Orbital diagram of diamondoid complexes with a NO ligand. (a) $^1$NO; (b) $^3$NO.

Furthermore, both carbon atoms of the carbonyl substituents have electronic communication with each other. It has been suggested that the carbonyl group is a weak σ donor [17] therefore, π back-bonding represents a way of reinforcing the links in carbonyl compounds. However, there is no back-bonding effect in the present case, therefore, the bond between carbon and iron must be weak, but these carbon atoms (joined to the iron center)

manifest some kind of phenomenon that reinforces their bonds producing a type of communication by constructing a "bridge" between the two carbon atoms, and this bridge hops over the iron center. This peculiar bond is also shown in Fig. 4a.

In this case the LUMO is a localized function, and is similar to the tetrahedral compound; it is found on the same atoms which are constituents of the HOMO. This effect would be interesting in
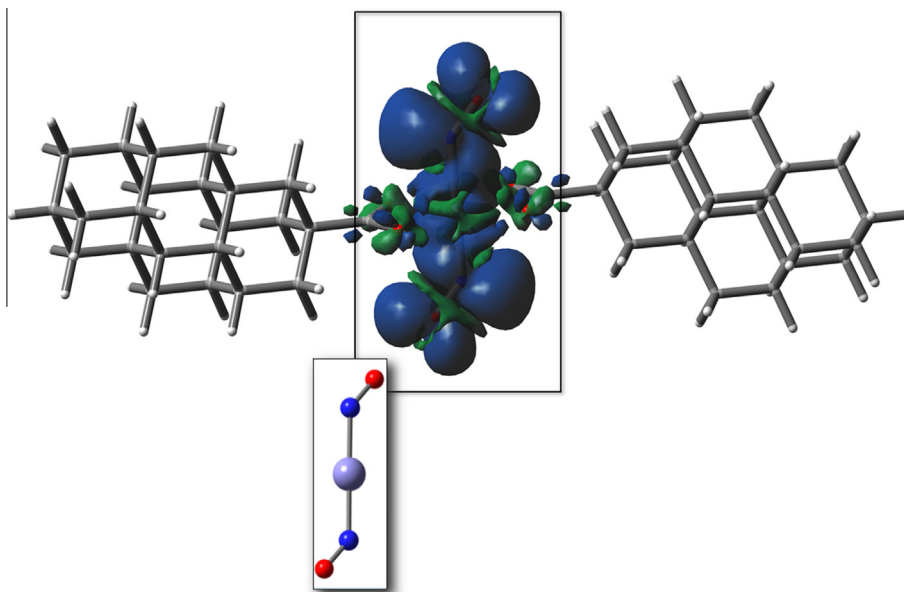
**Fig. 6.** Spin density map of the triplet state of the NO complex ($^3$NO).

a conducting molecule; but there are few probabilities of interesting electronic transfers in this case because they depend on two different mechanisms for electronic promotions.

The case of the $CN^{1-}$ ligand is completely different and the fundamental reason is the formal negative charges on the cyanide ligands. The HOMO and the LUMO have positive eigenvalues (see Fig. 4b); the energy gap is 2.43 eV which is characteristic of a semiconductor species; the HOMO is localized and centered on the metal and nitrogen atoms and makes a small contribution to the oxygen atoms. However, it is important to note that the LUMO is centered at the far edge of the diamondoid ligand; therefore reactivity is notably different because it can react in a nucleophilic process using the terminal nitrogen atoms.

## 8. NO complex

Nitrosyl complexes have been the object of strong and important studies because of their particular chemistry [18–20]. This radical manifests ubiquitous and chameleonic behavior that depends on its electronic count: it can act as a cation $NO^+$, a neutral free radical NO or an anion $NO^-$. In the first case, it is isoelectronic with CO, and its bonding participation should be identical or similar to that of CO, which has been described previously. However, the case is notably different.

In this case the strategy is to calculate the complex in three possible ways i.e., considering the ligand as a cation, in a neutral form and as an anion, and from this choose the best description. The result is interesting because the species with two positive charges cannot be stabilized; a calculation route shows a large increase in energy and the molecule becomes a breaking structure. The neutral case is particularly interesting because a stable structure is found in both possible multiplicities, i.e., the singlet and triplet states. Furthermore both states have practically identical energy values. Thus, there are clearly two structures; one with the paired "odd" electrons of each nitrosyl ligand and one with both electrons remaining in their respective nitrosyl groups and obviously unpaired. Based on the energy results, the situation can be described as a competitive situation between two states. The shape of this molecule and its corresponding molecular orbitals for the neutral singlet and neutral triplet states are shown in Fig. 5. The

singlet negative ion was analyzed, but the result shows that it is completely unstable and inaccessible to other configurations. The configurations of the neutral singlet and triplet states are shown in Fig. 5.

With respect to the molecule shape some aspects should be considered; the bent shape of the ligands and the separation of both with respect to the iron atom position. This situation leads to an S shape (see Fig. 6) comprising the groups that constitute the center of the molecule; the source of this phenomenon is the Enemark–Feltham model [21] which states that an excess of 6 or more electrons on the π configuration results in a bent structure.

Fig. 6 shows the spin density map for the triplet state of the nitrosyl complex. In this map, the equal distribution of unpaired electrons in oxygen for the two nitrosyl groups is observed.

## 9. Conclusions

Several compounds with an octahedral coordination sphere that contain two diamondoid ligands (joined by $COO^{1-}$ terminals) and symmetrical apical common substituent groups were simulated. The classical coordination groups i.e., water and ammonium, yield compounds with possible reactive positions in the diamondoid region. This feature makes it possible to prepare compounds with functionalized diamondoids. The CO and $CN^{1-}$ ligands cause notably different behavior when compared, despite their chemical similarities; in fact, the cyanide compound exhibits conductive characteristics. The nitrosyl derivative is the most intriguing compound because this ligand is known to display ionic or neutral species. The neutral case is stable but it can be a singlet or a triplet and these are able to coexist in almost the same population. Likewise, the NO group prefers the bent substitution despite the absence of charge.

In almost all cases the phenomenon named "nanodiamond effect" occurs, that is to say that diamondoid ligands on the equatorial positions of the complexes act as a potential barrier resulting in valence electrons becoming localized at the metallic center and the apical ligands. The general overview indicates that this kind of compound is of general interest for technological applications as they show wide versatility, ranging from insulators (water analogue) to strong semiconductors ($CN^{1-}$ analogue).

## Acknowledgements

## Appendix A. Supplementary material

Validation of computational method and Cartesian coordinates. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2015.12.021.

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